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COLORIMETRIC DETERMINATION OF ALKYL
NITRITES

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Sir: The Griess method (Saltzman procedure)¹ has been used in air pollution work to determine NO₂ in laboratory and field operations and it has been adapted for use in automatic instrumentation.² In this latter investigation² it was shown that alkyl nitrites also react with the reagent in the automatic nitrogen dioxide analyzer used.

It appeared of interest to determine the reactivity of the alkyl nitrites directly without also having to consider absorption efficiencies. The amount of reaction on a micromole basis of n-butyl nitrite, t-butyl nitrite, n-amyl nitrite, and i-amyl nitrite was determined for comparison with the reactivity of sodium nitrite and nitrogen dioxide.¹

The concentrations used ranged between 0.07 and 0.7 micromoles per 10 ml. of solution. The reproducibility of the results obtained ranged from ± 5 to ± 10 percent. The values obtained are given in Table I in terms of optical density per micromole of alkyl nitrite compared with that for sodium nitrite.

It has been shown previously that the reactivity of nitrogen dioxide compared with inorganic nitrite is in the ratio of 0.72 to 1. The values in Table I show that the alkyl nitrites investigated react at least to the same extent as nitrogen dioxide and generally more so. Distillation, particularly vacuum distillation, increases the

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Table I. Colorimetric Results with Alkyl Nitrites

Alkyl Nitrite	Method of Preparation	Optical Density Units/ μ Mole of Alkyl Nitrite ^a
		Optical Density Units/ μ Mole of NaNO ₂
n-Butyl nitrite	A	0.64 $\pm$ 0.04
	B	0.79 $\pm$ 0.05
	C	0.79 $\pm$ 0.07 ^b
t-Butyl nitrite	B	0.70 $\pm$ 0.03 ^c
<u>n</u> -Amyl nitrite	B	0.81 $\pm$ 0.04 ^c
	C	0.91 $\pm$ 0.04
<u>i</u> -Amyl nitrite	A	0.77 $\pm$ 0.06
	B	0.74 $\pm$ 0.04
	C	0.79 $\pm$ 0.03

A = untreated, B = atmospheric distillation, C = vacuum distillation.

^a Standard deviations given after average values, ^b average of three determinations, ^c average of two determinations.

indicated reactivity through improved purity of the alkyl nitrites.

If the alkyl nitrites are completely hydrolyzed and the nitrous acid reacts completely, and if the alkyl nitrites were completely pure, then the ratio of reactivity of alkyl nitrite to inorganic nitrite should be unity. It was observed in one experiment where one ml. of alkyl nitrite was diluted with 30 percent ethyl alcohol - water solution that the optical density of the reaction product was only 40 percent that in the acetic acid - water solution. This result could be due either to the repression of hydrolysis of the alkyl nitrite by excess alcohol or to repression of the subsequent reactions by the alcohol. Since a small amount of alcohol is produced in the hydrolysis itself, if the latter possibility were true, the ratio of reactivity of alkyl nitrite to inorganic nitrite would be reduced below one.

Undoubtedly, a portion of the difference in the observed ratios from unity is the result of appreciably less than 100 percent purity in the alkyl nitrites. High purity is difficult to achieve and maintain, owing to the instability of the alkyl nitrites to heat and light.

The results obtained in this investigation and elsewhere indicate that the method used for NO_2 is not specific to nitrogen dioxide but responsive to all compounds, inorganic and organic, containing the O - N - O group. These classes of compounds include the acyl peroxy nitrite found in the Los Angeles type atmospheres by infrared investigations.³ Furthermore, the complex reaction products formed by the reaction of nitric oxide and nitrogen dioxide with olefins often

contain reactive O - N - O groups in their structure. Consequently, methods are needed to differentiate NO_2 from organic nitrites.

EXPERIMENTAL DETAILS

The alkyl nitrites employed included n-butyl nitrite, t-butyl nitrite, n-amyl nitrite, and i-amyl nitrite obtained from commercial sources. These nitrites were subjected to atmospheric and vacuum distillations during various stages of the investigation. A number of the lots of alkyl nitrites used were dried over calcium chloride.

The solutions for the colorimetric determinations were prepared by dissolving one ml. of the appropriate alkyl nitrite in 75 ml. of glacial acetic acid and diluting to 250 ml. with distilled water. One ml. of this solution was diluted to 100 ml. with distilled water to make the necessary solutions in the microgram range. The analytical determinations were made on a Beckman Model DU Spectrophotometer using the procedure described by Saltzman.¹

The stability of 0.4 percent t-butyl nitrite in acetic acid - water solution was followed by means of the spectra in the 3000 - 4000 Å region using a Cary Model 11 Spectrophotometer. It was found that solutions kept at room temperature showed about 12 percent less absorption after 100 and 200 minutes. Solutions kept at iced water temperatures showed 4 percent decrease in absorption after 100 minutes and 8 percent decrease after 200 minutes. After 20 hours the solution at iced water temperature showed a 21 percent decrease.

An 0.004 percent t-butyl nitrite solution in acetic acid water was followed with Griess-Saltzman reagent. After 4 hours at 0° C. no change was observed, but after 20 hours, a 15 percent decrease was

found.

These results indicate that solutions in the range of several tenths of a percent can be kept for an hour or two at iced water temperatures without appreciable decomposition, but only for very limited periods of time at room temperature. At low concentrations, solutions at iced water temperatures are stable for many hours.

An undiluted alkyl nitrite was followed for several days after redistillation without any indication of decomposition.

It was necessary to keep all of the alkyl nitrite solutions in brown bottles or actinic flasks to prevent decomposition by light. If the working solutions had to be used for extended periods (more than one-half hour), they were kept in iced water baths. The undiluted alkyl nitrites were stored in brown bottles in the freezing compartment of a refrigerator.

LITERATURE CITED

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- (3) Stephens, E. R., et. al., J. Air Pollution Control Assn. 6, 159-165 (1956).

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